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Geometrical Structure buried in the Phase Space of Stochastic Structural Transition

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How systems climb through saddles from one basin to another in a multi-dimensional phase space of chemical reactions, or in general, how systems evolve on rugged energy landscapes with multiple saddles is one of the most intriguing subjects over the past several decades [1]. The introduction of the concept of “transition state (TS)” by Eyring [2] and Evans [3], and by Wigner [4] in 1930s has given us great successes in elucidating the kinetics and dynamics of not only chemical reactions [5, 6] but also structural transitions in clusters [7, 8] and in biomolecules like protein foldings [9], and the transport of asteroids in our solar system [10].

In the various forms of transition state theories (TST) [11, 12], it is assumed that the transition state, that is a dividing hypersurface in phase space, exists through which reacting species pass only once on the way from the reactants to the products before being “captured” in the products. It is also assumed that there exists a quasi-equilibrium between the reactant and a *system crossing the TS* from the reactant to the product [13]. The former and the latter have often been referred to the *no-return assumption* and the *local equilibrium assumption*, respectively. In the most frequently used form of the TST, the motions along the reaction coordinate at the transition state is treated as one-dimensional classical translational motion which is separable from the other degrees of freedom *at* the transition state. As previously pointed out [14], although the local equilibrium assumption has sometimes been referred as being occurred “between the reactant and the TS,” there is no source to yield a quasi-equilibrium between the reactant and the *dynamically separable*, elusive transition state. In other words, the dynamical approximation inherent in the TST implies that the reacting systems move about “ergodically” within the reactant more quickly than finding the reaction path *en route* to the TS.

However few theories have clarified the physical conditions required to validate these fundamental assumptions. The questions “in what circumstances can one extract the TS as

a no-return dividing hypersurface from the multi-dimensional phase space ?” and “what is the reaction path *en route* to the TS, i.e., path in the phase space along which all reacting species necessarily pass in order to climb from the reactant to the product?” are among the most elusive aspects in justifying the application of TST to a multitude of reacting systems. In practice, one has often defined the TS in configurational space with an *ad hoc* correction factor, called the transmission coefficient κ , to take into account that the system of interest actually makes more than one crossing through the surface presumed to be the desired dividing surface and/or that the system finds the reaction path *en route* to the TS nonergodically in the reactant.

Recent theoretical developments [15–23] in chemical reactions have greatly improved our understanding of the definability of a no-return dividing hypersurface and a reaction path along which all reacting species follow. By “lifting” the viewpoint in describing chemical reactions from the configuration space to the *multi-dimensional* phase space, we revealed [14–16], even for strongly coupled N degrees of freedom Hamiltonian systems, that the action associated with the reactive coordinate tends to stay invariant even up to energies high enough for the dynamics of the bath degrees of freedom to become chaotic in the region of index one saddle where only one degree of freedom is unstable (the reactive mode) while all the others are stable. The approximate invariant of motion associated with the reaction mode gives rise to a dividing hypersurface of co-dimension one (i.e., $(2N - 2)$ -dimension) which eliminates any recrossing occurring in the configuration space. The co-dimension one is the correct dimensionality for defining a TS to decompose the $(2N - 1)$ -dimensional equienergy space into two distinct regions, namely, the reactant and the product. We presented the natural reformulation [24] of the conventional TST based on that hypersurface in multi-dimensional phase space, and a practical algorithm [25] to visualize the dividing hypersurface in the multi-dimensional phase space of a given system. This enables us to envision the complicated pattern of recrossing trajectories in the configuration space and established a propensity rule [26] to predict *a priori* whether the system climbs through the saddle to the product, or returns to its original state. Our technique relies on the application of the Lie canonical perturbation theory (LCPT) [27], a classical analog of Van Vleck perturbation theory [28], to the regions of potential saddles. The robust existence of the dividing hypersurface even in a sea of chaos is due to the fact that the resonance condition, which usually spoils the perturbation scheme near elliptic equilibrium points due

to the small denominator problem [19, 20, 26, 29, 30], can never be satisfied among the pure imaginary frequency (associated with the reactive mode) and the real frequencies (associated with the bath mode) in the saddle region.

The theoretical developments [31–34] of classical unimolecular reaction rate theories based on the geometrical structures in the phase space had shed light on the definability of the no-return dividing hypersurface and the reaction paths or “tubes”, although most of them had essential difficulties in extending to systems with many-degrees (> 2) of freedom. For isomerization reactions with two-degrees of freedom, the so-called reactive island (RI) theory developed by De Leon, Marston, Mehta and De Almeida [33–36] provided us with an insightful clue to capture the global aspects of phase space geometrical structure from the invariants of motion in the *local* region of index one saddle. Based on the stable and unstable invariant manifolds of an unstable periodic orbit at the saddle, they presented a reaction conduit through which all reactive trajectories pass in the four-dimensional phase space (see also recent reviews [14, 37]). The earlier work of Wiggins [38] provided a firm mathematical framework of the geometrical structures of transports in multi-dimensional phase space, based on the notion of the normally hyperbolic invariant manifold (NHIM) and its stable and unstable manifolds as an appropriate generalization of the concept of “saddle” or “unstable periodic orbits” and “separatrices” in the multi-dimensional phase space. The major technical obstacle preventing Wiggins’ implementation, also the extension of the RI theory, to realistic multi-dimensional systems has been the lack of an algorithm for searching the NHIM in the regions of saddles. Quite recently, the LCPT was applied to the vicinity of saddles to extract the NHIM from many-dimensional phase space for a hydrogen atom in crossed electric and magnetic field (a 3 degrees of freedom system) [20] and the HCN/CNH isomerization process [21, 22, 39].

Despite of the important role it plays in the study of reaction dynamics in terms of phase space geometrical structures, the properties of NHIMs have still not been fully understood. To our best knowledge, the LCPT carried out so far in the construction of NHIMs in the literature normalized all degrees of freedom including both the reactive and bath modes. This means that the normalized Hamiltonian obtained is completely integrable near the saddle region. We will call such case as “full” LCPT. One advantage of the full LCPT is that the dynamics of the normalized coordinates can be solved exactly due to the integrability. However, one can easily see that the full LCPT fail to look deeply into the question of how

chaotic properties of NHIM affect the reaction dynamics, since it is well known that the on-set of chaos is caused by non-integrability and resonance overlapping in Hamiltonian dynamics [40]. Therefore, in order to explore the chaotic regime of NHIM and its stable/unstable manifolds, we carry out a modified normalization procedure in which only the reactive mode is normalized [41]. This means that the normalized Hamiltonian is cyclic only in the normalized coordinates associated with the reactive mode. We will call this normalization scheme as “partial” LCPT. Since resonance terms depending on the angle variables of the bath modes are kept, the partially normalized Hamiltonian is in general nonintegrable. One can then investigate various chaotic properties of NHIM and its stable/unstable invariant manifolds such as the transition to chaos and the breakdown of normal hyperbolicity.

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